

The University of Chicago

I

MOLECULAR REARRANGEMENT OF
TRIPHENYLMETHYLALKOXYAMINES

II

A REACTION BETWEEN DIETHYL ETHER
AND PHOSPHORUS PENTACHLORIDE

A PART OF A DISSERTATION SUBMITTED TO
THE FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1932

By

WALTER S. GUTHMANN

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UNIVERSITY OF CHICAGO]

MOLECULAR REARRANGEMENT OF TRIPHENYLMETHYL- ALKOXYAMINES*

WALTER S. GUTHMANN

Molecular rearrangements of triarylmethylhydroxylamines, $(\text{Aryl})_3\text{CNHOH}$ and $(\text{Aryl})_3\text{CNCH}_3(\text{OH})$ were investigated by Stieglitz and his collaborators.¹ The study of the rearrangement of triarylmethylalkoxyamines, $(\text{Aryl})_3\text{CNH}(\text{O-alkyl})$ was undertaken by us with the idea that the greater ease of following the alkoxy group in $-\text{NH}(\text{O-alkyl})$, as compared with the hydroxyl group in $-\text{NHOH}$, might shed further light on the mechanism of rearrangements of this general type.

Triphenylmethylmethoxyamine was first chosen for the study, but the *O*-benzyl $(\text{OCH}_2\text{C}_6\text{H}_5)$ derivative was later used as offering greater facility in tracing the fate of the alkoxy group in the reaction.

Only one other instance of the molecular rearrangement of an alkoxyamine derivative was found in the literature. Semper and Lichtenstadt² observed incidentally in 1914 that *O*-methyl benzophenone oxime is rearranged by concentrated sulfuric acid and yields a mixture of benzanilide, benzoic acid, aniline, and methyl benzoate. The triphenylmethyl derivatives have an advantage over ketoximes, aldoximes and acyl derivatives inasmuch as they contain no double bonds or other complicating structural details.

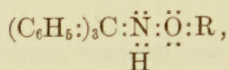
In triphenylmethylalkoxyamines we have the typical electronic molecular instability, or "fault," that is found in other rearranging hydroxylamine

* A portion of the dissertation submitted to the graduate faculty of The University of Chicago by Walter S. Guthmann, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

¹ Cf. STIEGLITZ AND LEECH, *J. Am. Chem. Soc.*, **36**, 272; STIEGLITZ AND STAGNER, *ibid.*, **38**, 2047 (1916); STAGNER, *ibid.*, **38**, 2069 (1916). For the electronic interpretation of the rearrangements see *ibid.*, **36**, 287 (1914); *Proc. Nat. Acad. Sci.*, **1**, 196 (1915); *J. Am. Chem. Soc.*, **38**, 2046 (1916) and **44**, 1293 (1922).

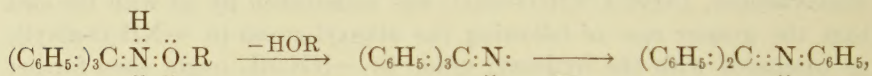
² SEMPER AND LICHTENSTADT, *Ber.*, **51**, 930 (1919). BRADY AND DUNN, *J. Chem. Soc.*, **129**, 2412 (1926), evidently overlooked this report of Semper and Lichtenstadt since they claimed that no such rearrangement had ever been observed, although they refer to the above article in another connection. Cf. BRADY, DUNN AND GOLDSTEIN, *loc. cit.*, p. 2387.

derivatives, chloro- and bromo-amines, hydrazines, azides, etc.³ The structure,[†]



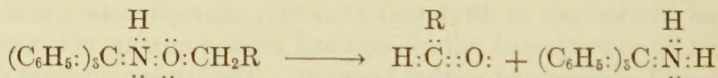
shows that the nitrogen and oxygen atoms together have only fourteen electrons—the electron-saturated atoms require eight each, or sixteen together. The inadequacy of a shared pair of electrons, completing the octets of each, was emphasized by Stieglitz⁴ as characteristic of all the above types of rearranging compounds. There is a shortage of two electrons which creates the “fault” in the molecule. This shortage of two electrons may lead to:

- (1) A molecular rearrangement,



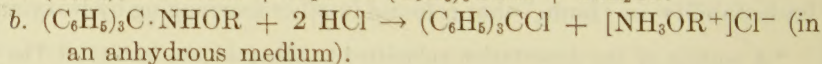
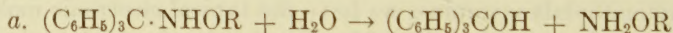
with *N*-phenyliminobenzophenone and an alcohol as the products of the action, the nitrogen and the oxygen atoms now having each its own complement of eight electrons.

- (2) The capture of two electrons on the part of the oxygen atom⁵ by the oxidation of the alkyl group:⁶



Triphenylmethanimine and an aldehyde are formed in this reaction.

- (3) Hydrolysis, or an equivalent decomposition, of the hydroxylamine derivative:



The present investigation has shown that molecular rearrangements of the type (1) anticipated do occur. The formation of aniline and of benzophenone, the characteristic products of rearrangement and subsequent

³ Cf. STIEGLITZ, *J. Am. Chem. Soc.*, **36**, 287 (1914) and **44**, 1293 (1922).

[†] $(\text{C}_6\text{H}_5)_3\text{C}^+\text{N}^-\text{H}^+$ represents the same structure with emphasis on the partial polarity of the individual atoms.

⁴ STIEGLITZ, *loc. cit.*, p. 1295 (1922).

⁵ Cf. STIEGLITZ, *J. Am. Chem. Soc.*, **36**, 279 (1914), on the electron structure of hydroxylamines.

⁶ Cf. L. W. JONES, *ibid.*, **36**, 1279 (1914), and his references to earlier work.

hydrolysis, was demonstrated. However, only a part of the substance undergoes rearrangement. In the case of the methoxy derivative, it is only a very small part, the predominating reaction leading to a breakdown of the compound to triphenylmethylcarbinol (3a) and decomposition products of methoxyamine. *N*-Triphenylmethyl-*O*-benzylhydroxylamine is rearranged much more readily—even by heat alone. The yields indicate a rearrangement of as much as 40 per cent. of the compound. At the same time, the formation of benzaldehyde results, probably from a primary oxidation of the benzyl radical (equation 2), although benzaldehyde might be formed by the oxidation of benzyl alcohol (equation 1), at the high temperature of the rearrangement by heat alone (420°).

It is interesting to note that the rearrangement can occur here even in the *absence of all reagents or salt-forming substances*, heat by itself being effective; but the yield is better when phosphorus pentoxide is used to promote the reaction, and the temperature required is far lower (160° instead of 420°). The free base, in the presence of phosphorus pentoxide, gives a better yield of the rearrangement products than does its hydrochloride under similar conditions.

We may summarize our results: if the hydroxyl group of triarylmethylhydroxylamine is replaced by the more stable methoxyl group, the tendency toward rearrangement is decreased. However, if conditions are made correspondingly more rigorous, rearrangement will again occur. When the *O*-benzyl group is used in place of the methoxyl, rearrangement is again easier. We have further shown that the tendency toward rearrangement exists, apparently residing in the electron deficiency within the hydroxylamino radical; but usually the tendency has to be aided, by the reagent most suitable in each case, toward promoting the primary formation of a rearranging univalent nitrogen derivative.

EXPERIMENTAL

Triphenylmethylmethoxyamine, $(\text{C}_6\text{H}_5)_3\text{CNHOCH}_3$.—Triphenylmethyl chloride (40 g. in 100 cc. of benzene) was rapidly added to methoxyamine* (20 g.), the mixture being well shaken under a reflux condenser. Heat was evolved. After the mixture had stood for twelve hours the precipitate of methoxyamine hydrochloride was removed by filtration; the filtrate, after evaporation of the benzene *in vacuo*, yielded 36 g. of triphenylmethylmethoxyamine (m.p. 89–90°). The product may be purified by recrystallization from ligroin (b.p., 60–80°), or by precipitation from a saturated benzene solution by ligroin (b.p., 40–50°). Soluble in ether, acetone, very soluble in benzene, and slightly soluble in ligroin, the pure compound was obtained in the form of white rhombic crystals, melting at 91.5–6°. It is quite stable, and may be kept indefinitely in a desiccator.

* Obtained from Eastman Kodak Co., dried over sodium sulfate and distilled.

Anal. Calc'd for $C_{20}H_{19}NO$: C, 82.88; H, 6.75; N, 4.84.

Found: C, 82.41, 83.17; H, 6.79, 6.79; N, 4.84, 4.76.

All attempts to prepare a benzoyl derivative of triphenylmethylmethoxyamine were unsuccessful.

Triphenylmethylmethoxyamine hydrochloride, $[(C_6H_5)_3CNH_2OCH_3]Cl$.—Dry hydrogen chloride precipitated the hydrochloride from a cooled benzene solution of the pure base as an extremely fine, gleaming white powder. Washed with ethereal hydrogen chloride and ligroin and dried *in vacuo*, it melts with decomposition at 179–180°.

Anal. Calc'd for $C_{20}H_{20}ClNO$: Cl^- , 10.86.

Found: Cl^- , 10.90, 10.95.

If the salt is allowed to stand *in vacuo* it dissociates into the free base and hydrogen chloride, as do the hydrochlorides of all the other known triphenylmethylhydroxylamines. If allowed to stand for a short time in an ether solution containing dry hydrogen chloride, the salt undergoes dissociation to triphenylmethyl chloride and methoxyamine hydrochloride (equation 3b).

Rearrangement of triphenylmethylmethoxyamine and its hydrochloride.—Twenty separate attempts to rearrange these compounds were made, but only five were successful. The first twelve (unsuccessful) attempts involved the use of ether* as the solvent for the reactants; varying amounts of phosphorus pentachloride, phosphorus pentoxide, thionyl chloride and barium oxide were used as agents. Both the free base and its hydrochloride were tried with these reagents. In all cases the original compound or triphenyl carbinol, or both, were recovered quantitatively. This proved that no migration of a phenyl group had occurred.

Negative results also attended the reaction when benzene was used as the solvent; but in carbon tetrachloride solutions migration of the phenyl group occurred to some extent. After hydrolysis of the reaction mixture with dilute hydrochloric acid, the carbon tetrachloride layer was separated, the solvent evaporated and the residue found to consist of triphenyl carbinol and benzophenone. The latter was separated as the sodium salt of its oxime. To this end the residue was heated under reflux for 1½ hours with hydroxylamine hydrochloride (1.5 g.) and sodium hydroxide (2 g.) in 20 cc. of dilute alcohol. Upon addition of water (100 cc.) to the solution, triphenyl carbinol was precipitated, collected and weighed. Dilute sulfuric acid precipitated the benzophenone oxime from the filtrate, quantitatively. A solution of triphenylmethylmethoxyamine (3 g.) and phosphorus pentachloride (5 g.) in 30 cc. of carbon tetrachloride yielded 0.2 g. of the oxime, melting at 140–1°. Pure benzophenone oxime melts at 143–4°; a mixture of the oxime obtained and the synthetic product melted at 141–2°. The identification of benzophenone proved that the molecular rearrangement (equation 1) had been effected.

Triphenylmethylmethoxyamine was next heated with phosphorus pentachloride in the absence of all solvents; the yield of benzophenone oxime was comparable to that obtained when carbon tetrachloride was used as solvent. Aniline could not be detected.†

* A reaction between phosphorus pentachloride and ether was observed and reported; WALTER S. GUTHMANN, *J. Am. Chem. Soc.*, **54**, 2938 (1932).

† LEECH, *J. Am. Chem. Soc.*, **35**, 1042 (1913), after confirming that aniline gives the well-known typical purple color with a half-saturated solution of calcium hypo-

When triphenylmethylmethoxyamine hydrochloride was heated with phosphorus pentoxide, only a trace of benzophenone was recovered from the hydrolysis products of the reaction mixture by the method outlined above. Triphenyl carbinol, however, was recovered in almost quantitative amounts.

Pyrolysis does not lead to the rearrangement of triphenylmethylmethoxyamine, which thus differs from *N*-triphenylmethyl-*O*-benzylhydroxylamine, discussed below. When the product of reaction was hydrolyzed and treated as above, no benzophenone and no aniline were found.

N-Triphenylmethyl-*O*-benzylhydroxylamine, $(\text{C}_6\text{H}_5)_3\text{CNHOCH}_2\text{C}_6\text{H}_5$.—A solution of triphenylmethyl chloride (40 g.) in 155 cc. of benzene was added to *O*-benzylhydroxylamine⁷ (45 g.), and the mixture was allowed to stand for two days. The reaction was quite slow and no perceptible amount of heat was evolved. The chlorine-free filtrate from the precipitate of *O*-benzylhydroxylamine hydrochloride yielded 45.5 grams of crude *N*-triphenylmethyl-*O*-benzylhydroxylamine (melting point 115–7°). Recrystallized three times from ligroin (b.p. 60–80°) the pure compound was obtained in the form of hard white rhombic crystals, melting at 118°.

Anal. Calc'd for $\text{C}_{26}\text{H}_{23}\text{NO}$: C, 85.42; H, 6.36; N, 3.84.

Found: C, 85.70, 85.50; H, 6.65, 6.42; N, 3.95, 3.75.

The hydrochloride of *N*-triphenylmethyl-*O*-benzylhydroxylamine is best prepared from a benzene solution of the base, by the addition of dry ethereal hydrogen chloride. The voluminous precipitate was washed with ethereal hydrogen chloride and dried *in vacuo*. It is a gleaming white powder, which softens at 152° and melts at 180–90° with decomposition.

Anal. Calc'd for $\text{C}_{26}\text{H}_{24}\text{ClON}$: Cl[−], 8.82.

Found: Cl[−], 8.11, 8.66.

The low results are probably due to loss of hydrogen chloride by the salt.

Rearrangement of N-triphenylmethyl-O-benzylhydroxylamine and its hydrochloride.—When *N*-triphenylmethyl-*O*-benzylhydroxylamine, or its hydrochloride, was heated with phosphorus pentachloride in benzene or carbon tetrachloride solution, the reaction followed the same general course as in the case of triphenylmethylmethoxyamine, except that very little color was noted in the hydrolysis product obtained from the reaction mixture.

The free base (3 g.) and phosphorus pentachloride (10 g.) were allowed to stand

chlorite, showed that methyl aniline gives with the same reagent a *blue* color, which fades in the course of about 15 seconds to a pale yellow color. The two compounds may be distinguished from one another by means of this test, provided they are not present in the same solution. Subsequent work on known solutions of aniline has shown that it does not give the hypochlorite color test in the presence of methoxyamine, even when an excess of the reagent is used. [Cf. STIEGLITZ AND BROWN, *J. Am. Chem. Soc.*, **44**, 270 (1922) and WEST, Doctorate Dissertation, University of Chicago, 1923, on the interference of ammonium salts with the aniline test.] However, even under these conditions it does give a good test by the method of DE PAOLINI, *Gazz. chim. ital.*, **60**, 859–62 (1930). De Paolini's test is also otherwise quite excellent, especially if carried out in 90% acetic acid; it is nearly as sensitive as the hypochlorite test and like the latter furnishes a means of distinguishing between aniline and methyl aniline, a fact not mentioned by De Paolini. It has the further advantage of functioning also in solvents other than water.

⁷ V. MEYER AND JANNY, *Ber.*, **15**, 1324 (1882); JANNY, *Ber.*, **16**, 170 (1883); BEHREND AND LEUCKS, *Ann.*, **257**, 206 (1890).

in carbon tetrachloride (30 cc.) for a day and then the mixture was boiled under reflux for one week. Hydrolysis of the product and subsequent treatment gave 0.3 g. of benzophenone oxime. No aniline was found.

The best yields of rearrangement products were obtained when *N*-triphenylmethyl-*O*-benzylhydroxylamine, or its hydrochloride, was mixed with phosphorus pentachloride and heated in an oil bath at 160°. Benzophenone, recovered from its oxime, synthetic benzophenone and the mixture of the two gave the same melting point, 48°. When bromine water was added to the acid portion of the original product of hydrolysis, tribromoaniline was precipitated. This was sublimed *in vacuo* and identified by its crystal form (needles), its melting point (118°) and by the melting point (118°) of a mixture of the compound and known tribromoaniline (118°).

A mixture of *N*-triphenylmethyl-*O*-benzylhydroxylamine hydrochloride (2.2 g.) and phosphorus pentoxide (3 g.) gave 0.65 g. of tribromoaniline (36% of the theoretical yield) and 0.25 g. of benzophenone oxime (23% of the theoretical yield).

N-triphenylmethyl-*O*-benzylhydroxylamine (2 g.) and phosphorus pentoxide (6 g.), when subjected to the same treatment, yielded 0.95 g. of tribromoaniline (60% of the theoretical yield) and 0.18 g. of benzophenone oxime (19% of the theoretical yield).

A mixture of *N*-triphenylmethyl-*O*-benzylhydroxylamine hydrochloride (3 g.) and phosphorus pentoxide (2 g.) heated to 445° for two minutes in a metal bath gave 0.75 g. of tribromoaniline (31% of the theoretical amount) and 0.18 g. of benzophenone oxime (12% of the theoretical amount). During the heating a few drops of material distilled out of the reaction vessel and were identified as benzaldehyde by the odor and by the formation of its sodium bisulfite addition product, which in turn was converted into benzaldehyde phenylhydrazone (m.p. 154°). A mixture of this product with known benzaldehyde phenylhydrazone (m.p. 156°) melted at 155°.

N-Triphenylmethyl-*O*-benzylhydroxylamine (2 g.) heated alone to 445° for two minutes, yielded 0.015 g. of tribromoaniline and 0.010 g. of benzophenone. The material that distilled during the heating proved to be chiefly benzaldehyde (identified as above) and ammonia.

The gums that remained after the hydrolyses in all the above experiments were not completely identified, but were found to contain small amounts of triphenyl carbinol, which was identified by its own melting point (162°) and the melting point of a mixture of it and known triphenyl carbinol (162°).

All tests for benzyl alcohol, benzoic acid, benzonitrile, and benzhydrol, among the products of the above rearrangements, were negative.

SUMMARY

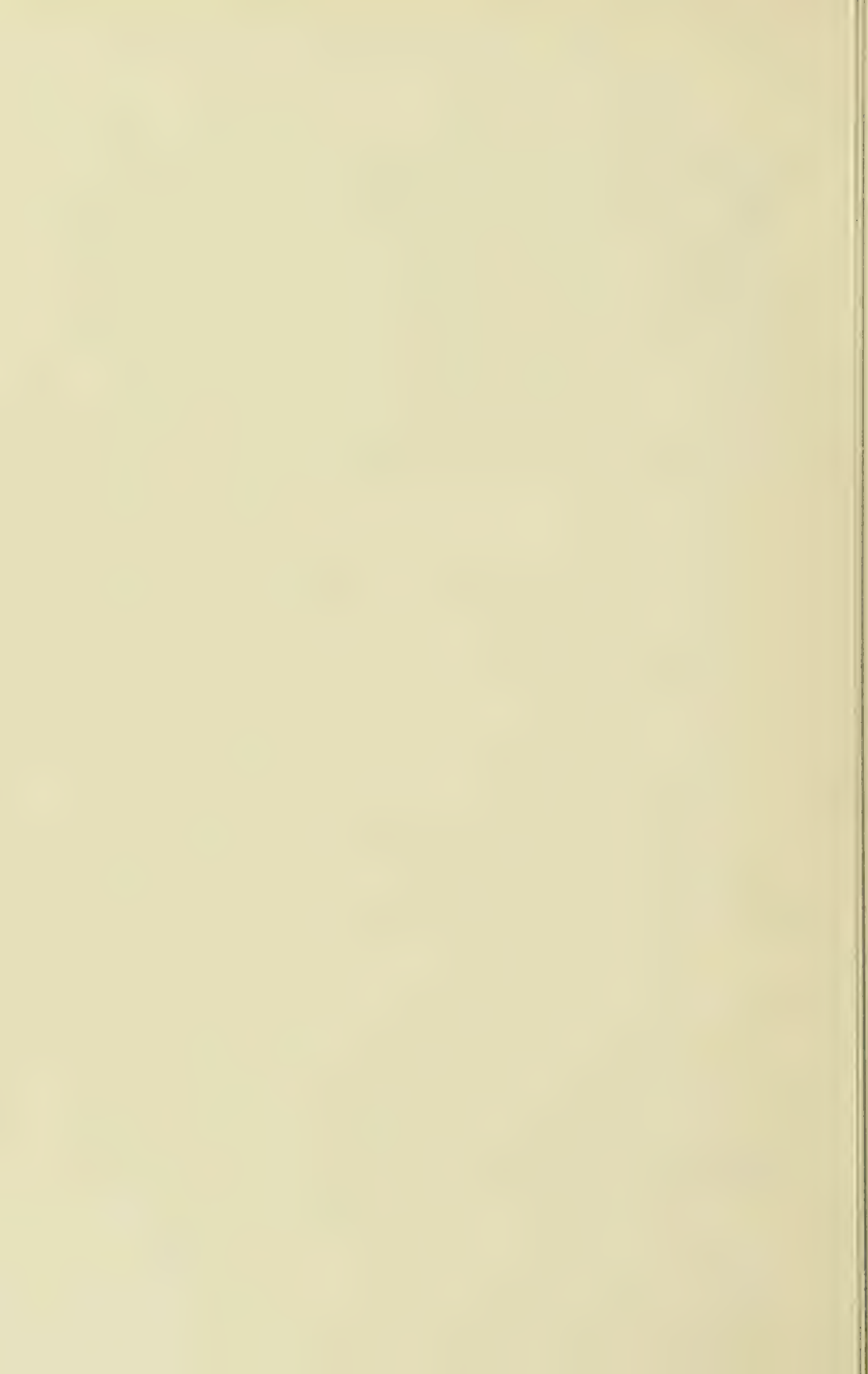
1. The preparation of triphenylmethylmethoxyamine and of *N*-triphenylmethyl-*O*-benzylhydroxylamine is reported.

2. The rearrangement of triphenylmethylmethoxyamine with phosphorus pentachloride was studied. In benzene and carbon tetrachloride solutions some rearrangement to *N*-phenyliminobenzophenone occurs, but the rearrangement goes very slowly and the yield of rearrangement products is very small. Other decompositions are paramount. These are discussed and demonstrated.

3. The rearrangement of *N*-triphenylmethyl-*O*-benzylhydroxylamine was brought about by phosphorus pentoxide at 160°, and by heat alone at 425°. The yields of rearrangement products, benzophenone and aniline, are very much better than in the case of the methoxyl derivative but not as good as in the rearrangement of triphenylmethylhydroxylamine. Intramolecular oxidation of the *O*-benzyl derivative to benzaldehyde was demonstrated.

4. The experimental results are interpreted on the basis of the Stieglitz theory of molecular rearrangements of this type.

I wish to express my sincere appreciation to Dr. Stieglitz for his invaluable guidance and help during the course of this work.



[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

A REACTION BETWEEN DIETHYL ETHER AND PHOSPHORUS PENTACHLORIDE

BY WALTER S. GUTHMANN¹

RECEIVED MARCH 11, 1932

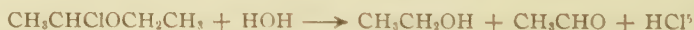
PUBLISHED JULY 6, 1932

In the course of some work on molecular rearrangements in the triphenylmethylhydroxylamine series, it was found necessary to reflux ether solutions of the materials being studied with phosphorus pentachloride for several days. At the end of this time water was added to the reaction mixture, and a very considerable and unexpected evolution of acetaldehyde was observed. This led to the investigation reported here.

Liebermann and Landshoff² report the formation of a crystalline compound of the probable formula $C_8H_{14}O_2P_3Cl_{15}$, when ether is treated with phosphorus pentachloride, and show that it is not a direct addition product with the formula $(C_4H_{10}O)_2 \cdot 3PCl_5$. No mention is made, however, of the evolution of acetaldehyde upon addition of water to the above compound.

Reactions of phosphorus pentachloride with aliphatic-aromatic ethers have been reported.³ In these cases only the aromatic portion of the molecule is oxidized.

It has been found that halogens, at ordinary temperatures, will react with ether to form α -halogen ethyl ethers which are easily hydrolyzed by water:⁴



It is well known that phosphorus pentachloride may be used as a chlorinating agent, and this fact might well account for the reaction described below, except that some organic phosphorus derivatives are formed at the

¹ A portion of the dissertation submitted to the graduate faculty of the University of Chicago, by W. S. Guthmann, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Liebermann and Landshoff, *Ber.*, **13**, 690 (1880).

³ Henri, *ibid.*, **2**, 710 (1869); Colson, *Compt. rend.*, **99**, 975 (1884).

⁴ Richter, "Organic Chemistry," P. Blakiston's Son and Co., Philadelphia, 1922, Vol. I, p. 129.

⁵ Since this paper was written, Henze and Murchison [*THIS JOURNAL*, **53**, 4077 (1931)], have reported the preparation of α -chloroethyl *n*-alkyl ethers by saturating equimolar quantities of paraldehyde, and the alcohol which contains the desired alkyl group, with hydrogen chloride, in the cold. The products hydrolyze very readily to re-form the original materials; on long standing they polymerize and leave a dark tarry residue.

same time (see experimental part). We might accept the point of view of Bergmann and Bondi,⁶ who advance evidence that one of the five chlorine atoms in phosphorus pentachloride is differently and less firmly linked than the others, which causes this compound to react as Cl-PCl_4 ; this would account for a C-P linkage in the product of reaction of phosphorus pentachloride with an organic compound.

The ultimate reaction product of phosphorus pentachloride with ether is an oil, not completely miscible with ether, and perfectly stable, at room temperatures, in the absence of moisture. All attempts to crystallize it have failed. On treatment with water the oil yields acetaldehyde, hydrochloric, phosphoric and phosphorous acids, and an unidentified organic residue which contains trivalent phosphorus. In view of the fact that the oil is most probably a mixture, no elementary analysis has been attempted. It is possible that this reaction provides an additional method for the preparation of the type of phosphoric and phosphorous esters prepared by Milobdendzki and Sachnowski⁷ and by Arbuzov and Arbuzuva.⁸

Further work in this field should yield valuable information on organic phosphorus compounds, and conceivably serve to develop a method for the determination of the relative ease of oxidation of the groups in mixed ethers.

Experimental Part

A mixture of pulverized phosphorus pentachloride (7 g.) and ether (30 cc.), carefully dried and purified, was boiled under reflux⁹ on the steam-bath for forty-eight hours, the reaction mixture being protected from moisture by means of a calcium chloride tube. At the end of this time a clear, almost colorless, mobile solution resulted. The reaction flask was well cooled and agitated while water (75 cc.) was slowly added to its contents. After separation from the aqueous layer, the ether layer was repeatedly washed with water. The washings were added to the original aqueous part. The presence of some organic phosphorous compound in the ether layer was shown as follows: the solution was dried over calcium chloride (or potassium carbonate), the solvent evaporated, and the residue oxidized with concentrated nitric acid; addition of molybdic acid then gave a precipitate, although no such precipitate was obtained prior to the oxidation.¹⁰

⁶ Bergmann and Bondi, *Ber.*, **64B**, 1455-80 (1931).

⁷ Milobdendzki and Sachnowski, *Chem. Polski*, **15**, 34 (1917); *cf. Chem. Abs.*, **13**, 2865 (1919).

⁸ Arbuzov and Arbuzuva, *J. Russ. Phys.-Chem. Soc.*, **62**, 1533 (1930); *cf. Chem. Abs.*, **25**, 2414 (1931).

⁹ The flasks used here were of 150-cc. capacity, and were joined to the condenser by means of a ground-glass joint in such a way that the condensed liquid washed the solid material (which otherwise tends to cake on the walls just above the surface of the reaction mixture) back into the bottom of the flask. These flasks also have the great advantage that contamination of the reaction mixture from stoppers is prevented.

¹⁰ Evaporation of the ether, prior to the hydrolysis, left an oil which did not crystallize on standing. Hydrolysis of this oil yielded the same products that were obtained from the ethereal solution.

The aqueous portion was fractionated; the fraction boiling below 35° contained all the acetaldehyde, which was identified by one of its many color reactions, and also by the preparation of the aldehyde semicarbazone¹¹ (melting point 162°). A mixture of the latter material with acetaldehyde semicarbazone from a known source had the same melting point (162°).

The distillation of the aqueous layer was continued until the volume of the material in the flask was reduced one-half; this residue was used for the following tests. (1) A portion allowed to stand exposed to air acquired a brown coloration, but no other change in properties was noted. (2) The presence of phosphate ion was shown by the molybdic acid reaction and confirmed by the precipitation of magnesium ammonium phosphate. When bromine was added to the filtrate obtained in the molybdic acid test, the yellow liquid became colorless, and some of the phosphorus was oxidized to phosphate ion, as was shown by the formation of more precipitate, an excess of molybdic acid having previously been used. (3) Ferric chloride was added to another portion, and the resulting mixture was made slightly alkaline and filtered. Addition of molybdic acid to a portion of the filtrate now gave no precipitate; but when another portion of the filtrate was oxidized with bromine or with concentrated nitric acid, the test for phosphate ion was positive.

The phosphate-free solution mentioned above has strong reducing properties when alkaline. It also gives the various tests for phosphorous acid, and we have the following indications of an organo-phosphorus compound: when the neutralized solution was evaporated a brown sirup resulted, encrusted with sodium chloride (formed in the neutralization of the hydrochloric acid originally present). This brown sirup was further heated, and first gave phosphine (identified in the usual way), and later became charred with the production of a distinct carbylamine odor, although no nitrogen was present. The residue which remained after the heating, when extracted with water, gave the usual phosphate tests; much carbon remained.

I wish to take this opportunity to express my sincere gratitude to Professor Stieglitz for his kind help and guidance.

Summary

1. A new reaction of diethyl ether and phosphorus pentachloride is described.
2. Organo-phosphorus compounds are formed in the course of the reaction. These are easily hydrolyzed by water alone.
3. The products of hydrolysis of the compounds mentioned in (2) include acetaldehyde, hydrogen chloride, phosphoric and phosphorous acids, and some unidentified stable organo-phosphorus compounds.

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¹¹ Thiele and Bailey, *Ann.*, **303**, 79 (1898).

